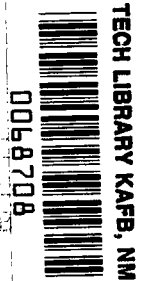


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*by V. I. Rodionova*

From *Uchenyye Zapiski Moskovskogo Gosudarstvennogo  
Pedagogicheskogo Instituta imeni V. I. Lenina*, Vol. 99, 1957.

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# ON THE DISSOLUTION OF ZINC IN ALKALIS

By V. I. Rodionova

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## ON THE DISSOLUTION OF ZINC IN ALKALIS

V. I. Rodionova

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The corrosion of zinc has been the subject of many investigations, but researchers have studied mainly the acid corrosion of zinc, the breakdown of zinc in water and in the atmosphere. The behavior of zinc in alkaline media has been paid very little attention.

The dependence of the dissolution of zinc on the alkali concentration has been studied only for certain concentrations of sodium hydroxide solutions, by the Soviet researchers Razumnikov, Gorbunov, and Daniyel'-Bek.

Razumnikov and Gorbunov [3] conducted investigations with elementary zinc in 10 %, 15 %, and 20 % solutions of sodium hydroxide. On the basis of their investigations they arrived at the conclusion that the corrosion of zinc in alkalis increases with increasing alkali concentration. The researchers do not explain how the rate of corrosion of zinc changes with increasing alkali concentration and what the cause of this change may be.

Daniyel'-Bek [1, 2] studied the dissolution of zinc in a broader range of concentrations of sodium hydroxide solutions -- 10 %, 20 %, 30 %, and 40 %. He points out that the extent of the corrosion of the metal decreases as the sodium hydroxide concentration is increased.

There is no information in the literature on the dissolution of zinc as a function of the concentration of such alkalis as KOH, LiOH, Ba(OH)<sub>2</sub>, and NH<sub>4</sub>OH.

On the basis of the available data on the behavior of zinc in alkalis, we undertook to investigate the relationship between the dissolution of zinc and the nature of the alkalis and the concentration of their solutions.

For the investigation, we used brand Ts-0 elementary zinc having the composition cited in the table.

The specimens were cut out of a single sheet of the metal and had an average area of 21 cm<sup>2</sup>.

TABLE 1

Chemical Composition of the Zinc Investigated in %

Brand of Zinc	Iron	Tin	Copper + cadmium	Lead	Antimony	Total, impurities	Zinc
Ts-0	0.008	0.001	0.015	0.01	None	0.034	99.966

The specimens were scoured by hand with emery paper No. 1, No. 2. After this the specimens were washed in alcohol and ether to remove water and grease and placed in a desiccator for a fixed interval of time.

Directly prior to the experiment the specimens were weighed. The experiment lasted for 2 hours, but other experiments were also conducted over other exposure times -- 4, 5, and 10 hours -- to determine the effect of the duration of pickling on the rate of dissolution of zinc in alkalis.

After the experiment, the specimens were washed with water with a soft brush to remove the corrosion products, dried with filter paper, and treated in alcohol and ether.

After a five-hour exposure in a desiccator, the specimens were weighed on an analytical balance. The loss in weight was calculated in  $\text{g/m}^2 \cdot \text{hr}$ .

Each experiment was conducted simultaneously on 5-7 specimens and repeated two to three times.

The investigation was performed in glass corrosimeters, without access to air and without mixing, in a thermostat at 20°C.

The following alkalis were used as the corrosion medium: NaOH, KOH, LiOH,  $\text{Ba}(\text{OH})_2$ ,  $\text{NH}_4\text{OH}$ , in solutions from 0.1 N up to almost saturated solutions.

The alkali solutions were prepared without access of carbon dioxide, since preliminary investigations showed that the presence of carbon dioxide reduces the corrosion rate of zinc.

The effect of the nature and concentration of the alkali on the rate of corrosion of zinc was investigated mainly by the gravimetric method.

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The results of the investigations are presented in Table 2 and in the graphs (Figs. 1, 2).

TABLE 2

Rate of Dissolution of Zinc in  $\text{g/m}^2 \cdot \text{hr}$  in Alkali Solutions  
at  $20^\circ\text{C}$  (Two-Hour Exposure)

Normality of alkali	NaOH	KOH	LiOH	$\text{Ba}(\text{OH})_2$	$\text{NH}_4\text{OH}$
0.1	0.260	0.324	0.298	0.333	0.230
0.2	-	-	-	0.318	-
0.3	-	0.326	-	0.307	-
1	0.292	0.332	0.317	-	0.480
2	-	0.258	-	-	0.470
3	0.307	0.244	0.289	-	-
4	0.298	0.238	0.246	-	0.430
5	0.289	0.231	-	-	-
6	0.286	0.253	-	-	0.420
7	0.286	0.256	-	-	-
10	0.271	0.256	-	-	0.360
13	0.235	-	-	-	-
14.4	-	-	-	-	0.360
19	0.209	-	-	-	-

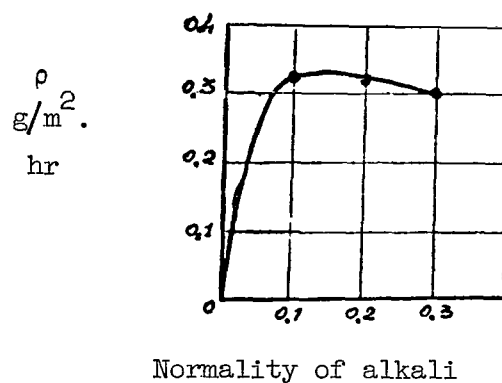


Fig. 1. Rate of corrosion of zinc in solutions of  $\text{Ba}(\text{OH})_2$  at  $20^\circ\text{C}$ .

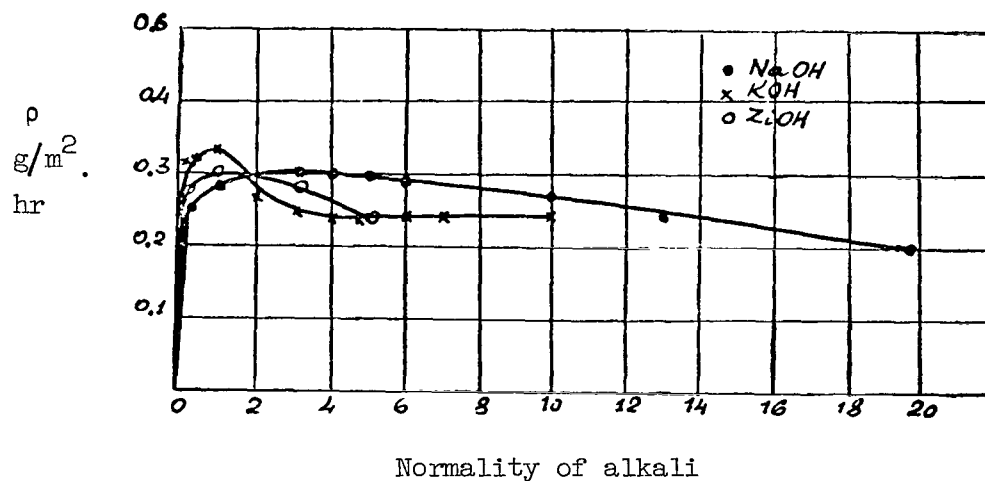


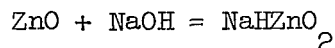
Fig. 2. Rate of dissolution of zinc as a function of the concentration of solutions of  $\text{NaOH}$ ,  $\text{KOH}$ , and  $\text{LiOH}$  at  $20^\circ\text{C}$ .

Investigation of the dissolution of zinc in solutions of NaOH, KOH, LiOH, and Ba(OH)<sub>2</sub> showed the presence of an induction

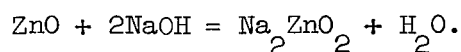
period with respect to the liberation of hydrogen, during which no visible changes occur in the metal; during this period there is no evolution of hydrogen, although the loss of metal is rather considerable.

The duration of this period depends on the nature and concentration of the alkali. The lower the concentration of the solution of a given alkali, the longer this period. In solutions of NaOH and KOH of the same concentration, the induction period is shorter for NaOH. This is attributable to the greater aggressiveness of sodium hydroxide solutions with respect to zinc, in comparison with potassium hydroxide solutions.

We believe that such a peculiarity of the dissolution of zinc in alkalis may be explained by the fact that during the first few minutes of the reaction of zinc with the alkali, the zinc oxide (which is always present on the surface of a specimen that has been in an air atmosphere) dissolves, forming the zincates:



or

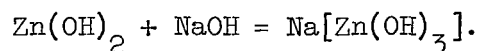


Experiments to determine the amount of hydrogen liberated in the pickling of zinc in various concentrations of sodium and a comparison of the ratio of the amount of hydrogen liberated to the amount of hydrogen equivalent to the dissolved zinc, have shown that in dilute solutions less hydrogen is liberated during the reaction than should be according to the stoichiometric calculations. The lower the concentration of the alkali solution, the greater this discrepancy.

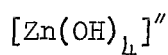
The dissolution of zinc in 0.1 N solutions of NaOH, KOH, and Ba(OH)<sub>2</sub> proceeds without visible evolution of hydrogen during the

entire time of the testing (2 hr).

We assume this happens so because in low concentrations of alkali, the reaction of zinc hydroxide with alkali proceeds with the formation only of the zincate:



In concentrated solutions of alkalis, on the other hand, as calculations have shown, the amount of hydrogen liberated is equivalent to the amount of zinc that dissolves, since in medium and concentrated solutions of alkalis the reaction of zinc hydroxide with the alkali proceeds with the formation of free hydrogen and complex ions with a coordination number 4 —



On examining the experimental data, we arrive at the conclusion that the corrosion rate of zinc depends on the nature of the cation and on the alkali concentration.

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The dependence of the corrosion rate of zinc on the alkali concentration is basically the same in all the alkalis we studied, with one small deviation.

In dilute solutions of alkalis (in solutions of sodium hydroxide from 0.1N to 3N, in solutions of potassium hydroxide and lithium hydroxide from 0.1N to 1N), the corrosion rate depends on the concentration of the aggressive medium. The higher the alkali concentration within these intervals, the higher the corrosion rate of the metal.

This is explained by the composition and properties of the surface compounds formed on zinc during pickling by the alkali.

According to the data of Feiknecht and Muller and our Soviet researchers Z. A. Iofa, S. Ya. Mirlina, and N. B. Moiseyeva, amorphous zinc hydroxide is formed on the surface of zinc in these concentrations of alkalis. Of all the known modifications of hydroxides, this is the most hydrated, the most soluble, and the most unstable. Dissolving in an alkali, it creates no protective barrier for the



metal, and hence the corrosion rate increases with increasing concentration of the aggressive medium.

In medium concentrations of alkali, the corrosion rate of zinc does not depend on the ion concentration of the aggressive medium. Under these conditions, all the unstable modifications of zinc hydroxide are converted to the one most stable, crystalline modification,  $E-Zn(OH)_2$ . It is firmly retained on the surface of the specimen and

prevents free influx of ions of the aggressive medium to the metal. Hence, in medium concentrations of alkali, the rate of corrosion of zinc is determined by the rate of formation of the protective layer of corrosion products.

The passivating action of the film formed on the surface of the specimen can be confirmed by experiments with mixing the solution, which we conducted for solutions of various concentrations of sodium hydroxide and potassium hydroxide.

The experimental findings are presented in Table 3 and Fig. 3.

The results of the investigations show that mixing the solution increases the corrosion rate of zinc in any concentrations of alkali. Mixing prevents the formation of a film of zinc hydroxide on the surface of the metal, since the corrosion products remain in the liquid phase in this case. In addition, mixing increases the diffusion of the reacting particles to the metal surface.

Our data agree with the data of Iofa, Mirlina, and Moiseyeva, who studied the passivation of zinc electrodes in galvanic cells and established that as the rate of mixing is increased, the critical current density, at which the electrode suddenly passes into the passive state, shifts in the direction of larger values.

In highly concentrated alkali solutions, the corrosion rate of zinc diminishes somewhat in comparison with the extent of corrosion in medium concentrations of alkalis.

On the basis of the investigations of Razumnikov, Gorbunov, Daniyel'-Bek, and Khal'mash (and our own findings), we conclude that this is a result of the influence of zincates, which are formed under these conditions. The solubility of the zincates decreases with increasing alkali concentration.

The dissolution of zinc in concentrated solutions of potassium hydroxide differs somewhat from the pattern observed for solutions of such alkalis as  $NaOH$ ,  $Ba(OH)_2$ , and  $LiOH$ .

The corrosion rate of zinc in concentrated solutions of potassium hydroxide is not lower than the corrosion rate in medium concentrations of alkali, but even somewhat greater. This may be explained by the data of Iofa, Mirlina, and Moiseyeva, who, on investigating the conditions of passivation of a zinc electrode during the operation

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TABLE 3

Rate of Corrosion of Zinc in  $\text{g/m}^2\cdot\text{hr}$  in Various Concentrations of KOH and NaOH with Mixing

Alkali concentration	Rate of mixing						
	Potassium hydroxide solutions				Sodium hydroxide solutions		
	Rate of dissolution				Without mixing	400 rpm	800 rpm
	Without mixing	400 rpm	800 rpm	1200 rpm			
0.1 N	0.315	4.26	6.78	9.63	0.260	-	6.28
0.3 N	-	-	-	-	-	0.63	-
1 N	0.332	-	7.03	11.32	-	-	-
3 N	0.234	1.53	2.87	2.99	0.307	1.63	1.97
5 N	0.236	-	2.07	2.21	-	-	-
7 N	0.265	0.70	1.60	-	0.286	-	1.01
10 N	0.240	0.68	1.29	1.22	0.271	-	0.495
19 N	-	-	-	-	0.209	-	0.424

of a galvanic cell by radiosopic and microscopic methods found that the rhombic modification of zinc hydroxide is formed on a zinc electrode in solutions of potassium hydroxide of medium concentrations at  $20^\circ\text{C}$ , and that it is precisely this modification that causes the passivation of the electrode. In concentrated solutions of potassium hydroxide, on the other hand, the stable and equilibrium form is non-hydrated zinc oxide, which does not give films that adhere tightly to the surface of the metal, and the electrode works without passivation. In our experimental data, this is expressed in the somewhat

greater value of the corrosion rate in concentrated solutions of potassium hydroxide.

A comparison of the aggressiveness of solutions of different alkalis reveals that the intensity of their action on zinc depends on their concentration.

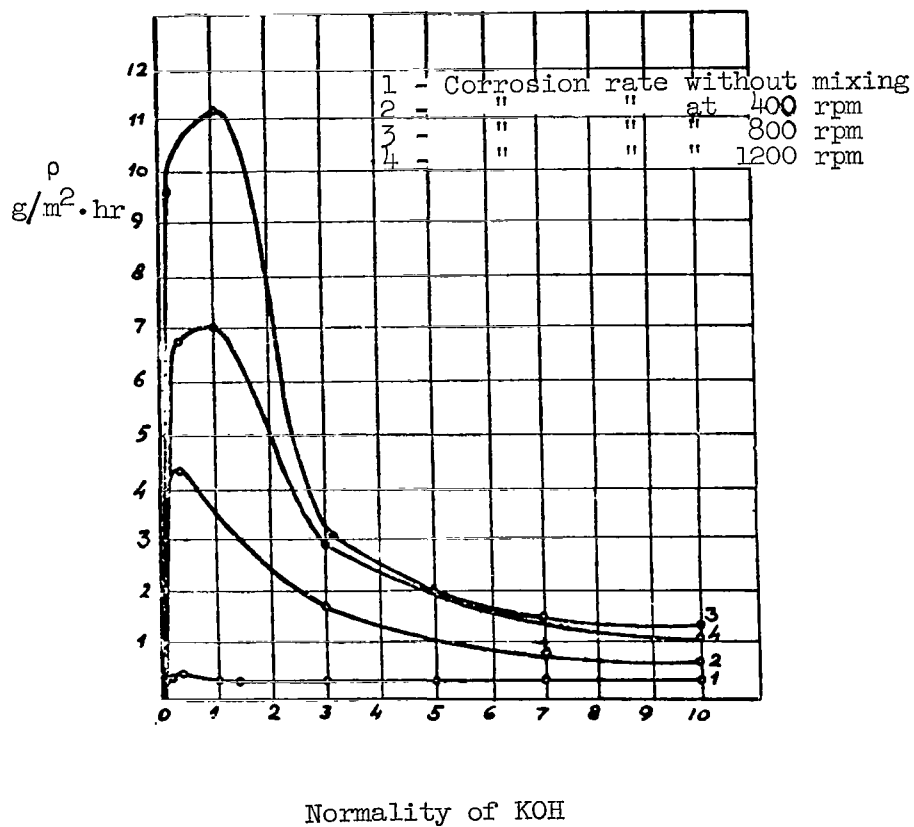


Fig. 3

Corrosion rate of zinc in solutions of potassium hydroxide at various rates of mixing.

For example, in 0.1 N solutions of alkalis, the rate of dissolution of zinc is higher in a solution of  $\text{Ba}(\text{OH})_2$ , then in NaOH,

LiOH, and KOH, in this order. One-normal solutions of these same alkalis are arranged in the following series with respect to their aggressiveness on zinc: KOH, LiOH, NaOH; in 4N solutions, the most aggressive is the solution of NaOH, then LiOH, KOH.

In solutions with higher concentrations, solutions of sodium hydroxide act more aggressively than solutions of potassium hydroxide of the same concentration.

Investigations of the dependence of the corrosion of zinc on the time of testing showed that the "Corrosion -- time" curve for a 1N solution of KOH runs below the "Corrosion -- time" curve for a 1N solution of NaOH. This is explained by the lower solubility of zinc oxide in solutions of potassium hydroxide of the same concentration and the lower solubility of potassium zincates in comparison with the solubility of sodium zincates in solutions of alkalis.

### CONCLUSIONS

1. The corrosion rate of zinc depends on the nature of the alkali cation.

2. In all the alkalis investigated, the dependence of the corrosion rate of zinc on the alkali concentration is almost identical. In dilute solutions of alkalis, the corrosion rate of zinc increases with increasing concentration of the aggressive medium, reaching a maximum in one-normal solutions of potassium hydroxide and lithium hydroxide and in a 3N solution of sodium hydroxide.

3. In medium concentrations of alkalis, the corrosion rate of zinc remains constant and does not depend on the ion concentration of the aggressive medium.

In concentrated solutions of most alkalis, the corrosion rate decreases somewhat.

The described dependence of the corrosion rate of zinc on the alkali concentration may be explained by the character of the surface compounds that arise during the reaction of zinc with alkali, their composition, structure, properties, and ability to persist on the surface of the metal.

4. The passivating action of the coating film is confirmed by

experiments on the mixing of the alkali solutions.

5. The corrosion of zinc in solutions of the investigated alkalis at 20° is uniform.

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